DERIVATION OF THE PHASE RULE

- A heterogeneous system in equilibrium of C components in which P phases are present.
- We have to determine the degrees of freedom of this system.
- Since the state of the system will depend upon the temperature and the pressure, these two variables are always there.
- The concentration variables depend upon the number of phases.
- Independent concentration variable for one phase with respect to the C components =C-1 (Since Conc. Of the last component is independent)
- Independent concentration variable for P phase with respect to the C components = P(C-1)
- Total number of variables = P(C-1) + 2
- On thermodynamic consideration when a system is in equilibrium, the partial molal free energy of each constituent of a phase is equal to the partial molal free energy of the same constituent in every other phase.
- Since the partial molal free energy of the constituents of a phase is a function of the temperature, pressure and (C – 1) concentration variables,
- it follows that if there is one component in two phases, it is possible to write one equation amongst the variables and if there is one component in three phases, this fact may be written with the help of two equations.
- In general, therefore, when P phases are present, (P – 1) equations are available for each component and for C components, the total number of equations or variables are C (P -1).

$$F = \text{No. of variables} - \text{Number of equations}$$

$$= [P (C - 1) + 2] - [C (P - 1)]$$

$$= PC - P + 2 - PC + C$$

$$= C - P + 2$$

$$F = C - P + 2$$

POLYMORPHISM

- The occurrence of the same substance in more than one crystalline forms is known a Polymorphism.
- In the case of elements the term allotropy is often used.
- The individual crystalline forms of an element are referred to as polymorphs or allotropes.

Enantiotropy

- one polymorphic form (or allotrope) can change into another at a definite temperature
- When the two forms have a common vapour pressure.
- This temperature is known as the transition temperature
- One form is stable above this temperature and the other form below it.
- When the change of one form to the other at the transition temperature is reversible, the phenomenon is called enantiotropy and the polymorphic forms enantiotropes.
- α-Sulphur to β-Sulphur

Monotropy

- It occurs when one form is stable and the other metastable
- The metastable changes to the stable form at all temperatures and the change is not reversible.
- There is no transition temperature as the vapour pressures are never equal.
- White phosphorus ⟶ Red phosphorus

Dynamic allotropy

- Resembles enantiotropy in that it is reversible but there is no fixed transition point.